

SCIENCE FOR GLASS PRODUCTION

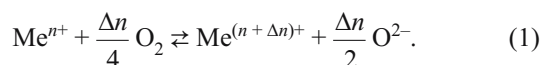
UDC 666.266.7.01:539.213.1

ACID–BASE INTERACTION OF THE COMPONENTS IN SODIUM–BOROSILICATE GLASSES

V. I. Kiyan¹ and A. B. Atkarskaya¹Translated from *Steklo i Keramika*, No. 7, pp. 3–7, July, 2007.

The effect of the coordination groups of boron, aluminum, and silicon on the acid-base properties of the glass mass and the change in the redox state of copper in boron-containing melts are studied. Indicators are proposed for evaluating the redox potential of the glass mass. The acid-base properties of commercial alkali-alumoborosilicate glasses are compared using these indicators.

Redox processes, occurring in melts, between elements with variable valence (EVV) play an important role in glass production technology. They are introduced into colorless or colored glasses according to the initial material (for example, iron and sulfur) or a colorant (chromium, copper, iron, and so on). In the glass mass they are always present in several valence states which are associated with redox equilibria of the type [1]



Uncontrollable shifts of the equilibrium (1) between the valence of EVV have a large and often negative effect on the technological (diathermancy, surface tension of melts) and spectral (coefficient of directed transmission of light) characteristics of glasses and change their operating properties and the technical and economic performance of industrial machines [2]. For this reason, to optimize technological processes or color a glass mass it is important to have quantitative expressions for evaluating the redox state of the glass mass. They must give information on the composition, structural features, and properties of glasses. Since glass is a complicated chemical compound, the fractional participation (additivity) of the components comprising the glassy matrix must be taken into account in the quantitative expressions.

The substantial difference, existing in any commercial glass, between the concentration of the basic components

(glass formers, modifiers) and impurity components (impurities from the initial materials and the decomposition of refractories, stains, fining agents, decolorants, gases) makes it possible draw an analogy, within the framework of inorganic chemistry, between a glass mass and a maximally diluted liquid solution [3, 4]. A silicate melt must be viewed as a solvent and the EVV impurities as the dissolved substance. Since the acidity (basicity) of a solvent, evaluated quantitatively by the pH (pOH), determines the valence-coordination state of a dissolved substance, the salient behavior of EVV in a glass mass can be viewed from the standpoint of the concept of acid–base relations [4].

The modern picture of the nature of acid-base interaction of the components in solutions is based on the theory of Lewis acids and bases [3]. According to this theory, a base is any compound (atoms, ions, radicals, molecules) that can contribute an electron pair for forming a covalent bond (for example, the ion OH^- in water solutions) and an acid is any compound that accepts this pair.

The activity of the ions of free oxygen O^{2-} , which do not enter into silicon – oxygen groups, can serve as a measure of the basicity determining the acid-base properties of multi-component silicate melts. These ions are distinguished from other ions (bridging ions O^0 and nonbridging ions O^-) by a high mobility and the highest activity and are electron donors. It is believed [1] that O^{2-} form as a result of the thermal dissociation of alkaline silicates according to the scheme



¹ Berezhichi Glass Works, Kaluga Oblast, Russia; Branch of the V. G. Shukhov Belgorod State Technological University, Novorossiisk, Russia.

TABLE 1.

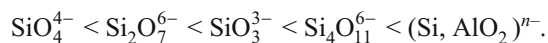
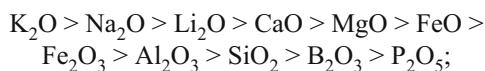
Value of φ	Coordination group			
	BO_4^{5-}	AlO_4^{5-}	BO_3^{3-}	AlO_6^{9-}
$\varphi > 1$	Present	Present	Absent	Absent
$1 > \varphi > 0.33$	"	"	Present	"
$0.33 > \varphi > 0$	Absent	"	"	"
$\varphi < 0$	"	Absent	"	Present

Among other hypotheses about the nature of the basicity of silicate glasses, the following notions should be noted:

anions of free oxygen with silicon–oxygen ($[\text{SiO}_{3/2}]^+$, $[\text{OSiO}_{3/2}]$) and boron – oxygen ($[\text{BO}_{3/2}]^+$, $[\text{OBO}_{3/2}]$) groups which perform acidic (positive) and basic (negative) functions coexist in melts [4];

free oxygen O^{2-} is completely absent in high-silica melts [1].

The latter fact made it necessary to find and develop correlation relations between the acid-base properties of melts and the parameters characterizing the chemical interaction of MeO in structural groups (apparent molar refraction of oxygen, degree of bond ionicity, electronegativity — EN) [5], and so forth. The calculation of the EN of metal oxides and crystalline silicates made it possible to arrange them in a series with monotonically increasing acidity (decreasing basicity): the higher the EN, the stronger the acidic properties are [5]:



The interrelationship of acid-base and redox processes has an important place in the concept of acid-base relations. According to M. I. Usanovich's hypothesis [3], covalent bond formation with sharing of electrons between substances occurs in the first processes and the second processes are distinguished by a high degree of electron transfer from a reduc-

ing agent to an oxidizing agent, and therefore they are a particular case of an acid–base interaction.

Since a reliable and simple method of determining the acid-base properties of a glass mass for application under production conditions has not been developed, and considering the interrelationship of acid–base and redox processes, impurity EVV are widely used as indicators to make an indirect evaluation of the basicity of melts [2, 6]. A shift of the equilibrium in the direction of higher valence indicates an increase of basicity (decrease of acidity) of the glass mass and vice versa.

The objective of the present work is to select an indicator for making a quantitative evaluation of the acid-base properties of melts and to study the effect of the coordination state of the structural groups formed in glass on the position of the EVV equilibrium in a glass mass.

Glasses belonging to the alkali-alumoborosilicate system, which is the basis for optical, chemical-laboratory, phototechnical, electrovacuum, medical, and other types of glasses possessing high chemical and heat resistance, are investigated. The groups SiO_4^{4-} , BO_3^{3-} , BO_4^{5-} , AlO_4^{5-} , and AlO_6^{9-} and are present in the structure. The coordination state of boron and aluminum is related with the quantity φ [1]

$$\varphi = \frac{\text{Me}_2\text{O} - \text{Al}_2\text{O}_3}{\text{B}_2\text{O}_3},$$

where Me_2O , Al_2O_3 , and B_2O_3 are the molar contents of the oxides of alkali metals, aluminum, and boron (%).

The relationship between φ and the coordination state of boron and aluminum in glasses is shown in Table 1 [1].

For positive φ the coordination of boron with respect to oxygen varies from 3 to 4. For negative values the coordination number of aluminum increases from 4 to 6. We note that these structural transformations are confirmed by Raman scattering and x-ray spectral analysis [7].

The compositions of the glasses studied in the A_i and B series (according to synthesis), the molar content of boron and aluminum indifferent coordination states, the values of φ , and certain indicators characterizing the redox properties are presented in Table 2. The three series A_i are sections with

TABLE 2.

Series	Change of the molar content of the structural groups, * %								Indicator ranges		
	SiO ₂	Na ₂ O	Al ₂ O ₃			B ₂ O ₃			φ	EN _{eff}	K _b
			total	of which		total	of which				
				AlO ₄ ⁵⁻	AlO ₆ ⁹⁻		BO ₄ ⁵⁻	BO ₃ ³⁻			
A ₂₀	74.0 – 30.0	3.0 – 25.0	3.0	25.0	Absent	20.00	Absent	20.00	0.0	1.79 – 1.43	0.19 – 2.51
A ₁₅	78.16 – 62.96	3.4 – 11.0	3.4	11.0	"	15.04	"	15.04	0.0	1.80 – 1.65	0.20 – 0.70
A ₁₀	83.73 – 63.53	4.1 – 13.2	4.1	13.2	"	10.07	"	10.07	0.0	1.79 – 1.63	0.24 – 0.96
B	68.8	5.6 – 9.6	5.6 – 1.6	5.6 – 1.6	"	20.0	0.0 – 7.0	20.0 – 13.0	0.0 – 0.4	1.73 – 1.67	0.33 – 0.66

* The boron and aluminum content in different structural forms was calculated in the manner described in [1].

constant molar content of boron anhydride i , equal to 10, 15, or 20%, and the Na_2O content = Al_2O_3 ; for this reason, here $\varphi = 0$. The series B contained 20% B_2O_3 , and the amount of sodium and aluminum oxides varied so that the value of φ increased from 0 to 0.4.

Copper and chlorine dopants introduced in strictly constant concentrations were chosen as the indicators of the change in the acid-base characteristics of the glasses. The fact (known from reference data) that the optical density of copper-colored glass at the wavelength 790 nm is proportional to the content of the oxidized form of Cu^{2+} was taken into account. Univalent copper in the compound CuCl absorbs at $\lambda = 380$ nm, and metallic (reduced) copper Cu^0 exhibits a band at 600 nm. The procedure for synthesizing glasses and investigating properties are presented in [8].

The acid-base properties of the glasses were evaluated using the following:

the effective electronegativity [9]:

$$\text{EN}_{\text{eff}} = (\sum \text{EN}_i a_i) / \sum a_i,$$

where EN_i is the electronegativity of electropositive elements (cations) in glass and a_i is the atomic content of the cation (5), and the coefficient of glass basicity [10] developed at the D. I. Mendelev Russian Chemical Technology Institute

$$K_b = \frac{4.6C_1 + 4.7(C_2 - C_1)}{0.82C_3 + 1[C_4 - (C_2 - C_1)]}, \quad (2)$$

where C_1 , C_2 , C_3 , and C_4 are, respectively, the molar content of aluminum, sodium, silicon, and boron oxides in glass (%).

The optical density at wavelength 790 nm (D_{790}) as function of the effective electronegativity and the coefficient of basicity of the series A_{20} and B are presented in Fig. 1. It is evident that D_{790} (and the content of oxidized Cu^{2+}) increases as K_b increases and EN_{eff} decreases. Therefore, the basicity of the glasses is directly proportional to the coefficient of basicity and inversely proportional to the effective electronegativity.

For the series A_{20} a shift of the equilibrium in the direction of oxidized copper and therefore an increase of the basicity of the glass mass correlate with a decrease of the SiO_4^{4-} concentration and an increase of the AlO_4^{5-} content (see Table 2 and Fig. 2). A similar phenomenon is also observed for the series A_{10} and A_{15} , but the slope angle of the straight lines A_{10} and A_{15} with respect to the abscissa is smaller than that of A_{20} . This could be due to the higher basicity of the A_{20} glasses because of their high content of boron anhydride. Correspondingly, the oxidation of copper in the highly basic A_{20} melts stops. For B series compositions the growth of the basicity is due to the increase of the concentration of BO_4^{5-} groups due to a decrease of BO_3^{3-} and AlO_4^{5-} groups.

The optical density of A series glasses at wavelength 380 nm (D_{380}), which is proportional to the concentration of

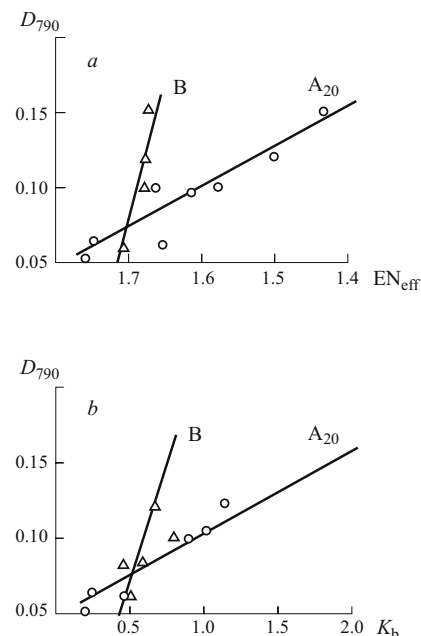


Fig. 1. Variation of the optical density of glasses at the maximum of the absorption band of Cu^{2+} (D_{790}) as a function of the coefficient of basicity (a) and the effective electronegativity (b).

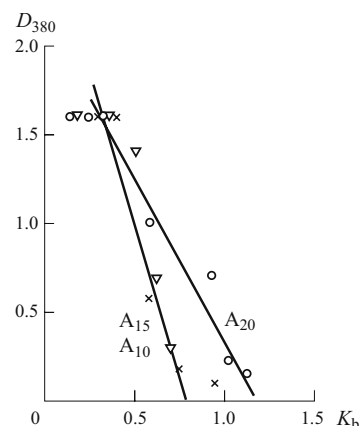


Fig. 2. Variation of the optical density of glasses at the maximum of the absorption band of CuCl (D_{380}) as a function of the effective basicity.

univalent copper, is compared in Fig. 2 with the values of K_b . Here, D_{380} decreases in a regular manner as the coefficient of basicity increases. Figures 1 and 2 show that silicon, boron, and aluminum structural groups have different acid-base properties. An increase of the content of four-fold coordinated boron and aluminum effectively decreases the acidity of melts. The effect of SiO_4^{4-} is weaker; BO_3^{3-} intensifies acidity. It is known [11] that with respect to their effect on the increase of basicity (decrease of acidity) the structural units form a series which correlates well with the parameters characterizing the salient features of the chemical bond (for

TABLE 3.

Sample	Molar content, %*			K_b	Optical density at wavelength, nm		CLTE, 10^{-7} K^{-1}	Glass color
	SiO_2	Al_2O_3	Na_2O		790	380		
1	30.0	25.0	25.0	2.51	0.15	0.07	92.0**	Green
2	68.8	1.6	9.6	0.60	0.12	1.20	66.0	"
3	68.8	5.6	5.6	0.33	0.06	1.60	52.3	Colorless
4	76.8	1.6	1.6	0.09	0.05	1.07	40.6	Red

* The B_2O_3 content was 20.0% in all cases.

** Computed.

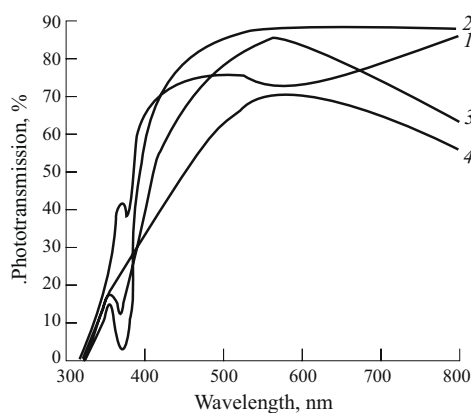


Fig. 3. Spectral phototransmission curves of glasses 1, 2, 3, and 4) $K_b = 0.09, 0.33, 0.66$, and 2.51 , respectively.

example, the bond strength and the intensity of the cation field):

Group	$\text{BO}_3^{3-} > \text{SiO}_4^{4-} > \text{BO}_4^{5-} > \text{AlO}_4^{5-} > \text{NaO}_6^{6-}$				
Strength of the ordinary Me – O bond, kJ/mole	523	426	393	387	84
Cation field intensity	1.63	1.57	1.34	0.96	0.19

On this basis, it is best to use K_b to evaluate the basicity of glass since K_b takes account of the structural changes of boron and aluminum: the concentrations of the groups with

TABLE 4.

Composition [7]	K_b	Indicator [8]			
		CLTE, 10^{-7} K^{-1}	heat resistance, °C	dielectric losses, 10^{-4}	permittivity
No. 17	0.28	39.5	230	22	4.2 – 4.7
ZC-9	0.36	35.5	200	28	4.2 – 4.6
ZS-8	0.40	48.0	220	32	No data
ZS-5	0.53	49.0	180	40	5.35
S-88-13	2.40	89.0	130	45	No data

the most basic properties AlO_4^{5-} (C_1) and BO_4^{5-} ($C_2 - C_1$) are summed in the numerator in the expression (2) and the concentrations of the more acidic SiO_4^{4-} (C_3) and BO_3^{3-} [$C_4 - (C_2 - C_1)$] are summed in the denominator. When using the effective electronegativity, these transformations are not taken into account.

Some properties of the four glass groups studied are compared in Table 3, and Fig. 3 displays the spectral phototransmission curves of the glasses.

The glass No. 1 ($K_b = 2.51$) is green, its optical density is maximum at 790 nm and equals 0.15, indicating the presence of oxidized copper Cu^{2+} . The more acidic glass No. 2 ($K_b = 0.60$) is also green but in contrast to the composition No. 1 a band at 380 nm is observed in its spectrum; this band is due to copper in the form of the compound CuCl . As K_b decreases further to 0.33 in glass No. 3, the glass becomes colorless, the increase of the absorption at $\lambda = 380$ nm indicates an even larger shift of the redox equilibrium $\text{Cu}^{2+} \rightleftharpoons \text{Cu}^+ \rightleftharpoons \text{Cu}^0$ in the Cu^+ direction. Finally, the ultra-acidic composition No. 4 ($K_b = 0.09$) promotes further reduction and part of the Cu^+ transforms into Cu^0 . The red hue of the glass and the appearance of a band near 600 nm serve to confirm this.

It is evident from Table 3 that the basicity index is related with not only the spectral but also the physical properties of the glass. The CLTE increases from 40 to $92 \times 10^{-7} \text{ K}^{-1}$ for K_b ranging from 0.09 to 2.51.

Since commercial boron-containing glasses, as a rule, have positive values of ϕ at 790 nm, K_b can be used to predict the effect of compositions on the direction of the redox equilibria of EVV and some characteristics (thermal, electrical) of glasses. As an illustration, some properties and parameters of commercial electrovacuum glasses are presented in Table 4.

In contrast to the glass S-88-13 with $K_b = 2.40$, the compositions with high acidity are founded and fired at a higher temperature, have low CLTE, high heat resistance, low dielectric losses, and low permittivity.

In summary, the criteria developed on the basis of the concept of acid-base relations make it possible to evaluate objectively the character of the change in the acid-base pro-

perties of melts in diverse technological processes. They have been used successfully to develop compositions of copper-halide photochromic glasses, investigate the dynamics of the variation of the diathermancy of melts with the introduction of founding accelerators [12], and optimize glass-making under conditions of continuous production of sheet glass.

REFERENCES

1. A. A. Appen, *Glass Chemistry* [in Russian], Khimiya, Leningrad (1974).
2. V. I. Kiyan, É. K. Polokhlivets, P. A. Krivoruchko, and A. B. Atkarskaya, "Redox potential of the glass mass in a continuous technological process," *Steklo Keram.*, No. 11, 10 – 12 (1999).
3. K. Dale and J. Selbin, *Theoretical Inorganic Chemistry* [Russian translation], Khimiya, Moscow (1976).
4. M. M. Shul'ts, "Acid-base concept in application to oxide melts and D. E. Mendeleev's teaching concerning the glassy state," *Fiz. Khim. Stekla*, **1**(2), 129 – 138 (1984).
5. A. A. Appen, *Heat-Resistance Inorganic Coatings*, Khimiya, Leningrad (1967).
6. V. I. Kiyan, P. A. Krivoruchko, and A. B. Atkarskaya, "Internal reserves for increasing the efficiency of glass-making furnaces," *Steklo Keram.*, No. 8, 8 – 11 (1999).
7. M. V. Artamonova, V. V. Gorbachev, V. I. Kiyan, et al., "Acid-base properties of photochromic glasses with negative ϕ_B ," in: *Institute Proceedings, D. I. Mendeleev Moscow Chemical Technology Institute* [in Russian], Issue 146, Moscow (1987), pp. 55 – 58.
8. V. I. Kiyan, V. F. Solinov, and M. V. Artamonova, "Application of naturally occurring raw materials for obtaining photochromic glasses with CuCl," *Steklo Keram.*, No. 12, 12 – 13 (1985).
9. A. B. Atkarskaya, L. I. Demkina, and G. A. Nikolaeva, "Absorption spectra of iron in silicate optical glasses," *Fiz. Khim. Stekla*, **8**(4), 451 – 455 (1982).
10. M. V. Artamonova, V. I. Kiyan, and Yu. I. Mashir, "Evaluation of the acid-base properties of sodium-alumoborosilicate glasses," *Fiz. Khim. Stekla*, **12**(6), 731 – 733 (1986).
11. A. A. Appen, V. B. Glushkova, and S. S. Kayalova, "Calculation of the binding energy of oxides," *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, **1**(4), 576 – 582 (1969).
12. V. I. Kiyan, Yu. I. Mashir, and A. B. Atkarskaya, "Changing the redox potential of a glass mass by introducing a founding accelerator into the batch," *Steklo Keram.*, No. 3, 5 – 7 (2000).